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(54) A method of coating articles with an abrasion-resistant porcelain-enamel and aticles produced by the method

(57) In order to provide on a metal substrate a coating having a degree of hardness up to 7 and even higher according to MOHS or DIN 51 150, class A-AA with the same energy as the conventional porcelain-enamel- and glaze method the following components in percentages by weight

from 10% to 70% Al_2O_3 Aluminium oxide
from 10% up to 30% SiO_2 Silicon oxide
up to 5% V_2O_5 Vanadium pentoxide
up to 5% P_2O_5 Phosphorus pentoxide
up to 12% R_2O Alkali metal oxide
up to 20% ZrO_2 Zirconium oxide
up to 20% TiO_2 Titanium oxide

are sintered together at temperatures between 800°C and 1000°C, cooled-down, the glassy solidified mass is milled to desired fineness, blended with porcelain enamel or glaze frits up to 50% by weight, proper mill additions being added, the substrate is dipped or flowed in the slip or slip is sprayed thereon, this coating is then fired at a temperature, depending on the substrate material, between 550° and 1200°C.

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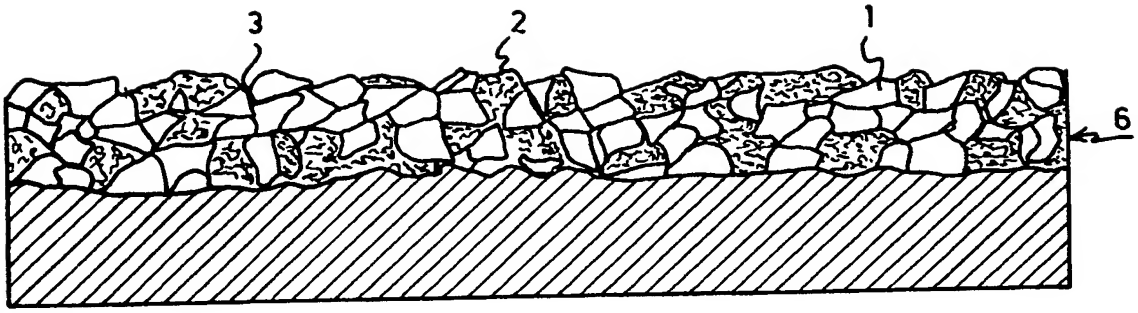

FIG. 1

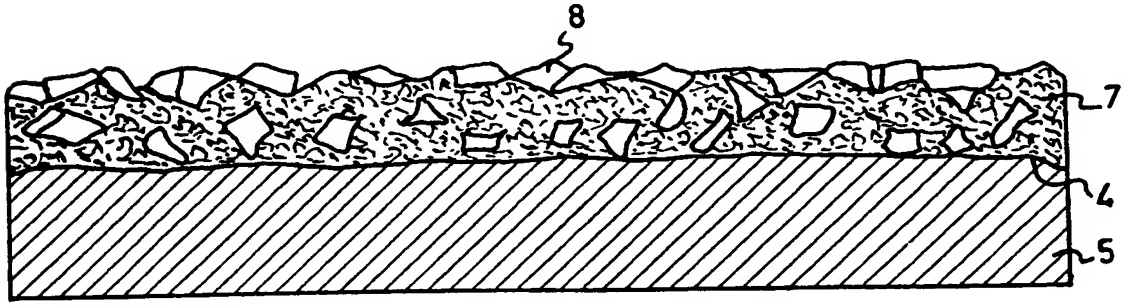

FIG. 2

SPCIFICATION

A method of coating articles with an abrasion-resistant porcelain-enamel and articles produced by the method

Method of manufacturing a highly abrasion-resistant, acid-resistant, porcelain-enamelled or glazed coat, on a metal or china and earthenware surface, as well as articles coated with such a coat.

The invention relates to a method of manufacturing a highly abrasion-resistant, acid-resistant, porcelain-enamelled coat on a metal surface, e.g. on stainless steel, sheet-iron, aluminium-base alloys and cast-iron, or a glazed coat on china, earthenware and stoneware, as well as articles coated with it, such as all kinds of table tops and work surfaces, wall panels, floor tiles, window sills, stove tops, kitchen sinks, rinsing tubs, shower basins, bathtubs, hot plates, articles for cooking, frying and baking, as well as tools, including files, and grinding wheels.

It is known practice to enamel the surface of articles made of metal and also to glaze the surface of articles made of china or earthenware. In both cases a pleasant, distinguished, smooth surface is reached. A disadvantage of this known method is that all surfaces coated in this way are not sufficiently abrasion-resistant. The fact is that this conventional enamel or glaze coat has a degree of hardness not exceeding 6, according to MOHS, and can easily be damaged or scratched by small quartz grains in the size of sand grains, or by unglazed china or ceramic articles, which have a degree of hardness of 7 according to the MOHS scale and the coated articles become worn out completely in the course of time.

It is an aim of the present invention to provide a metal, china or earthenware surface as a carrier, with a highly abrasion-resistant, acid-resistant, enamel or glaze coat, with a degree of hardness up to 7 and higher according to MOHS, as well as according to DIN 51 150, class A-AA, whereby the expenditure of energy does not exceed that of the conventional porcelain-enamel and glaze method.

According to the present invention there is provided a method of manufacturing a highly abrasion-resistant, acid-resistant, porcelain-enamelled coating on a metal surface, e.g. on stainless steel, sheet-iron, aluminium-base alloys and cast-iron, or a glazed coating on china-ware, earthenware and stoneware, wherein percentages by weight

from 10% to 70%	Al_2O_3	Aluminimoxide
from 10% to 30%	SiO_2	Siliconoxide
up to 5%	V_2O_5	Vanadiumpentoxide
up to 5%	P_2O_5	Phosphor pentoxide
up to 12%	R_2O	Alkali oxide
up to 20%	ZrO_2	Zirconium oxide
up to 20%	TiO_2	Titanium oxide

are sintered together at a temperature between 800°C and 1000°C.

The cooled down, glassy solidified, sintered mass then has to be milled to the desired fineness, blended with usual porcelain-enamel or glaze frits up to 50% by weight; the proper mill additions added; the to be coated surfaces of the carrier can then be applied in the well known way of either dipping or flowing in this slip or by spray application with this slip; then firing of this coat on the carrier surface at a temperature, depending on the carrier material, between 550° and 1200°C. Practically the alkali oxide contents (R_2O) of the sintered mass may have the following date in percentages by weight:

up to 12%	Na_2O	Sodium oxide
up to 10%	K_2O	Potassium oxide
up to 5%	Li_2O	Lithium oxide

The admixture of a sinter-smelt composed in this way to a porcelain enamel frit for metal or a glaze frit for china and earthenware enables the production of acid-resistant enamel-or glaze surfaces according to DIN 51 150, i.e. testing of the resistance against cold citric acid, class A-AA, which means that the surface is not, or hardly visibly attached by citric acid, with extremely high abrasion-resistance, as the main part of the aluminium oxide is a crystal of the α-phase present in this sinter-smelt.

For articles for which an acid-resistant coating is not necessary, thus a highly abrasion-resistant coating is sufficient, only aluminium oxide of the α-phase is added to the usual enamels or glazes. To reach a highly abrasion-resistant anti-slip coating, e.g. for bathtubs and shower basins or floor coverings, suitable coarse-milled sinter material is added to the enamel or the glaze.

To manufacture tools, such as files, grinding- or emery wheels, an adequate carrier, provided for this purpose, is profitably coated in the same way with an enamel or glaze coating with coarse-milled sinter material. This coarse coating is also suitable for the inside of frying pans and casseroles, as well as stewing pans, as with this coat, as tests have shown, as soon as they are filled with fat and thus the micro top structure is filled with fat, the boiling, frying or baking ware does not stick to the pan, even at extremely high temperatures.

Special attention is drawn to the fact that the multi-crystalline structure itself of such enamels and glazes is

insensitive to thermal shocks.

An embodiment of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a cross section of a coated carrier before fixing;

Figure 2 is a similar view to Figure 1 after the carrier has been subjected to a firing process.

Referring now to the drawings in detail a sinter smelt 1 is milled, wet or dry, with the usual enamel or glaze frits 2 preferably in the ratio of 1 : 1 parts by weight, with the usual mill additions 3 to the fineness necessary for the use to which the article to be coated is put.

In this way the mass is smashed, depending on the particle-size distribution and is maintained as a heterogeneous mixture of enamel or glaze frits on the one hand and the sinter-smelt on the other hand. Coating of the surface 4 of a carrier 5 to be enamelled or glazed can take place in the usual way by dipping, flowing or spraying. Figure 1 shows a cross-section of the structure of such a mixture 6 in the unfired condition. During the firing, which takes place, depending on the material of the carrier, e.g. aluminium-base alloys, cast-iron, sheet-iron, stainless steel, earthenware and stoneware, between 550°C and 1200°C, the enamel frit or glaze frit particles including the usual mill additions fuse together with the particles of the sinter smelt to a multi-crystalline enamelling 7 or glazing.

The α-phase of the aluminium oxide 8 is maintained and, as found, this is pushed to the surface and distributed homogeneously. The protruding articles of the mix will now protect the porcelain-enamelled or glazed surface substantially against mechanical and, if necessary, also chemical influences.

CLAIMS

1. A method of manufacturing a highly abrasion-resistant, acid-resistant, porcelain-enamelled coating on a metal surface, e.g., on stainless steel, sheet-iron, aluminium-base alloys and cast iron, or a glazed coating on chinaware, earthenware and stoneware, wherein percentages by weight

from 10% to 70%	Al_2O_3	Aluminiumoxide
from 10% to 30%	SiO_2	Siliconoxide
up to 5%	V_2O_5	Vanadium pentoxide
up to 5%	P_2O_5	Phosphor pentoxide
up to 12%	R_2O	Alkali oxide
up to 20%	ZrO_2	Zirconium oxide
up to 20%	TiO_2	Titanium oxide

are sintered together at a temperature between 800°C and 1000°C, after sintering the cooled-down, glassy solidified mass is milled to the desired fineness, blended with porcelain enamel or glaze frits up to 50% by weight; the proper mill additions are then added, the carrier surfaces are dipped or flowed in the slip or the slip is sprayed on the carrier, this coating is then fired on the carrier surface at a temperature, depending on the material of the carrier, between 550° and 1200°C.

2. A method as claimed in claim 1, wherein the alkali oxide contents (R_2O) of the sintered mass may have the following data in percentages by weight:

up to 12%	Na_2O	Sodium oxide
up to 10%	K_2O	Kalium oxide
up to 5%	Li_2O	Lithium oxide.

3. A method as claimed in claim 1, wherein before or after milling only aluminium oxide of the α-phase is added to the enamels or glazes.

4. A method as claimed in claim 1, wherein coarse-milled sinter material is added to the enamels or glazes.

5. A tool, especially a grinding tool, wherein the working surface of an article formed as a file or a grinding wheel is coated by the method claimed in any of claims 1 to 4.

6. An article of cooking,frying or baking ware, the inside surface of which has been coated by the method claims in any of claims 1 to 4.

7. A method of manufacturing a highly abrasion-resistant, acid-resistant, porcelain-enamelled coating on an article, substantially as herein described with reference to the accompanying drawings.

8. An article having a highly abrasion-resistant, acid-resistant, porcelain-enamelled coating according to the method of claim 1, substantially as herein described with reference to the accompanying drawings.

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